

SYLLABUS FOR CHEMISTRY PAPER-I & II FOR MANIPUR CIVIL SERVICES COMBINED COMPETITIVE (MAIN) EXAMINATION

PAPER-I

1. Atomic structure

Quantum theory, Heisenberg's uncertainty principle, Schrodinger wave equation (time independent). Interpretation of wave function, particle in one-dimensional box, quantum numbers, hydrogen atom wave functions. Shapes of s, p and d orbitals.

2. Chemical bonding

Ionic bond, characteristics of ionic compounds, factors affecting stability of ionic compounds, lattice energy, Born-Haber cycle; covalent bond and its general characteristics, polarities of bonds in molecules and their dipole moments. Valence bond theory, concept of resonance and resonance energy. Molecular orbital theory (LCAO method); bonding in homonuclear molecules: H_2^+ , H_2 to Ne_2 , NO, CO, HF, CN, CN^- , BeH_2 and CO_2 . Comparison of valence bond and molecular orbital theories, bond order, bond strength and bond length.

3. Solid State

Forms of solids, law of constancy of interfacial angles, crystal systems and crystal classes (crystallographic groups). Designation of crystal faces, lattice structures and unit cell. Laws of rational indices. Bragg's law. X-ray diffraction by crystals. Close packing, radius ratio rules, calculation of some limiting radius ratio values. Structures of NaCl, ZnS, CsCl, CaF_2 , CdI_2 and rutile. Imperfections in crystals, stoichiometric and nonstoichiometric defects, impurity defects, semi-conductors. Elementary study of liquid crystals.

4. The gaseous state

Equation of state for real gases, intermolecular interactions, liquefaction of gases and critical phenomena, Maxwell's distribution of speeds, intermolecular collisions, collisions on the wall and effusion.

5. Thermodynamics and statistical thermodynamics

Thermodynamic systems, states and processes, work, heat and internal energy; first law of thermodynamics, work done on the systems and heat absorbed in different types of processes; calorimetry, energy and enthalpy changes in various processes and their temperature dependence.

Second law of thermodynamics; entropy as a state function, entropy changes in various process, entropy–reversibility and irreversibility, Free energy functions; criteria for equilibrium, relation between equilibrium constant and thermodynamic quantities; Nernst heat theorem and third law of thermodynamics.

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Micro and macro states; canonical ensemble and canonical partition function; electronic, rotational and vibrational partition functions and thermodynamic quantities; chemical equilibrium in ideal gas reactions.

6. Phase equilibria and solutions

Phase equilibria in pure substances; Clausius-Clapeyron equation; phase diagram for a pure substance; phase equilibria in binary systems, partially miscible liquids—upper and lower critical solution temperatures; partial molar quantities, their significance and determination; excess thermodynamic functions and their determination.

7. Electrochemistry

Debye-Huckel theory of strong electrolytes and Debye-Huckel limiting Law for various equilibrium and transport properties.

Galvanic cells, concentration cells; electrochemical series, measurement of e.m.f. of cells and its applications fuel cells and batteries.

Processes at electrodes; double layer at the interface; rate of charge transfer, current density; overpotential; electroanalytical techniques—voltameter, polarography, amperometry, cyclic-voltammetry, ion selective electrodes and their use.

8. Chemical kinetics

Concentration dependence of rate of reaction; differential and integral rate equations for zeroth, first, second and fractional order reactions. Rate equations involving reverse, parallel, consecutive and chain reactions; effect of temperature and pressure on rate constant. Study of fast reactions by stop-flow and relaxation methods. Collisions and transition state theories.

9. Photochemistry

Absorption of light; decay of excited state by different routes; photochemical reactions between hydrogen and halogens and their quantum yields.

10. Surface phenomena and catalysis

Absorption from gases and solutions on solid adsorbents, adsorption isotherms,—Langmuir and B.E.T. isotherms; determination of surface area, characteristics and mechanism of reaction on heterogeneous catalysts.

11. Bio-inorganic chemistry

Metal ions in biological systems and their role in ion-transport across the membranes (molecular mechanism), ionophores, photosynthesis—PSI, PSII; nitrogen fixation, oxygen-uptake proteins, cytochromes and ferredoxins.

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12. Coordination chemistry

(a) Electronic configurations; introduction to theories of bonding in transition metal complexes. Valence bond theory, crystal field theory and its modifications; applications of theories in the explanation of magnetism and electronic spectra of metal complexes.

(b) Isomerism in coordination compounds. IUPAC nomenclature of coordination compounds; stereochemistry of complexes with 4 and 6 coordination numbers; chelate effect and polynuclear complexes; trans effect and its theories; kinetics of substitution reactions in square-planar complexes; thermodynamic and kinetic stability of complexes.

(c) Synthesis and structures of metal carbonyls; carboxylate anions, carbonyl hydrides and metal nitrosyl compounds.

(d) Complexes with aromatic systems, synthesis, structure and bonding in metal olefin complexes, alkyne complexes and cyclopentadienyl complexes; coordinative unsaturation, oxidative addition reactions, insertion reactions, fluxional molecules and their characterization. Compounds with metal-metal bonds and metal atom clusters.

13. General chemistry of 'f' block elements

Lanthanides and actinides; separation, oxidation states, magnetic and spectral properties; lanthanide contraction.

14. Non-Aqueous Solvents

Reactions in liquid NH_3 , HF , SO_2 and H_2SO_4 . Failure of solvent system concept, coordination model of non-aqueous solvents. Some highly acidic media, fluorosulphuric acid and super acids.

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Paper-II

1. **Delocalised covalent bonding** : Aromaticity, anti-aromaticity; annulenes, azulenes, tropolones, kekulene, fulvenes, sydnones.

2(a) **Reaction mechanisms** : General methods (both kinetic and non-kinetic) of study of mechanism or organic reactions illustrated by examples—use of isotopes, cross-over experiment, intermediate trapping, stereochemistry; energy diagrams of simple organic reactions—transition states and intermediates; energy of activation; thermodynamic control and kinetic control of reactions.

(b) **Reactive intermediates** : Generation, geometry, stability and reactions of carbonium and carbonium ions, carbanions, free radicals, carbenes, benzyne and nitrenes.

(c) **Substitution reactions** : S_N1 , S_N2 , S_Ni , $S_N1/$, $S_N2/$, $S_Ni/$ and $SRN1$ mechanisms; neighbouring group participation; electrophilic and nucleophilic reactions of aromatic compound including simple heterocyclic compounds—pyrrole, furan thiophene, indole.

(d) **Elimination reactions** : $E1$, $E2$ and $E1cb$ mechanism; orientation in $E2$ reactions—Saytzeff and Hoffmann; pyrolytic **syn** elimination—acetate pyrolysis, Chugaev and Cope eliminations.

(e) **Addition reactions** : - Electrophilic addition to $C=C$ and $C\equiv C$; nucleophilic addition to $C=O$, $C\equiv N$, conjugated olefins and carbonyls.

(f) **Rearrangements** : Pinacol-pinacolone, Hoffmann, Beckmann, Baeyer–Villiger, Favorskii, Fries, Claisen, Cope, Stevens and Wagner–Meerwein rearrangements.

3. **Pericyclic reactions** : Classification and examples; Woodward-Hoffmann rules—electrocyclic reactions, cycloaddition reactions [2+2 and 4+2] and sigmatropic shifts [1, 3; 3, 3 and 1, 5] FMO approach.

4. **Chemistry and mechanism of reactions** : Aldol condensation (including directed aldol condensation), Claisen condensation, Dieckmann, Perkin, Knoevenagel, Witting, Clemmensen, Wolff-Kishner, Cannizzaro and von Richter reactions; Stobbe, benzoin and acyloin condensations; Fischer indole synthesis, Skraup synthesis, Bischler-Napieralski, Sandmeyer, Reimer-Tiemann and Reformatsky reactions.

5. Polymeric Systems

(a) **Physical chemistry of polymers** : Polymer solutions and their thermodynamic properties; number and weight average molecular weights of polymers. Determination of molecular weights by sedimentation, light scattering, osmotic pressure, viscosity, end group analysis methods.

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(b) **Preparation and properties of polymers** : Organic polymers—polyethylene, polystyrene, polyvinyl chloride, Teflon, nylon, terylene, synthetic and natural rubber. Inorganic polymers—phosphonitrilic halides, borazines, silicones and silicates.

(c) **Biopolymers** : Basic bonding in proteins, DNA and RNA.

6. **Synthetic uses of reagents** : OsO_4 , HIO_4 , CrO_3 , $\text{Pb}(\text{OAc})_4$, SeO_2 , NBS, B_2H_6 , Na-Liquid NH_3 , LiAlH_4 , NaBH_4 , $n\text{-BuLi}$, MCPBA.

7. **Photochemist** : Photochemical reactions of simple organic compounds, excited and ground states, singlet and triplet states, Norrish-Type I and Type II reactions.

8. Principles of spectroscopy and applications in structure elucidation

(a) **Rotational spectra**—diatomic molecules; isotopic substitution and rotational constants.

(b) **Vibrational spectra**—diatomic molecules, linear triatomic molecules, specific frequencies of functional groups in polyatomic molecules.

(c) **Electronic spectra** : Singlet and triplet states. $\text{N} \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions; application to conjugated double bonds and conjugated carbonyls—Woodward-Fieser rules.

(d) **Nuclear magnetic resonance** : Isochronous and anisochronous protons; chemical shift and coupling constants; Application of ^1H NMR to simple organic molecules.

(e) **Mass spectra** : Parent peak, base peak, daughter peak, metastable peak, fragmentation of simple organic cleavage, McLafferty rearrangement. molecules;

(f) **Electron spin resonance** : Inorganic complexes and free radicals.